

1,189,746



# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Improvements in or relating to a Photosensitive Titanium Dioxide

We, NATIONAL LEAD COMPANY, a Corporation organised under the laws of the State of New Jersey, United States of America, of 111 Broadway, New York 10006, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the preparation of a titanium dioxide which possesses photo-sensitive properties.

Many types of photosensitive materials are used in photographic and copy paper systems. Among these are carbon black and zinc oxide. Carbon black, although possessing excellent conductive properties, has little or none of the photoreactive properties necessary for use in copy paper systems, while zinc oxide, although used with limited success, has low opacity in copy papers.

Although most commercial grades of titanium dioxide pigment possess a slight amount of photo-reactivity, it is insufficient to be useful in copy paper systems. However, the particular titanium dioxide composition produced by the present invention is not a pigmentary grade material, but is specifically designed to have a high degree of photoreactivity and opacity in copy paper systems and hence is especially useful in the copy paper industry.

The photoreactive titanium dioxide powder of the present invention has the crystal structure of anatase and comprises finely divided particles having an average individual particle size from 100 to 500 angstroms; a sulphur

[Price 5s. Od.]

content, calculated as percent S, which falls within the range of from 0.03% to 0.3% on a dry  $TiO_2$  weight basis; possesses a surface area from 60 to 250 sq. meters per gram; a moisture content from 2% to 10% and a photoreactivity measured by the mandelic acid test herein-after described as a change in reflectance of at least 5 units in 2 minutes when exposed to ultraviolet radiation.

This type of photoreactive titanium dioxide is prepared by the process of the present invention which comprises: hydrolyzing a titanium sulphate-iron sulphate solution to form hydrous titanium oxide, filtering, bleaching and washing said hydrous oxide to remove the soluble iron salts therefrom, said bleached hydrous oxide being substantially iron-free but containing from 5% to 15%  $H_2SO_4$  associated with said hydrous oxide, forming an aqueous slurry of said bleached hydrous oxide, treating said slurry with a sufficient amount of ammonium hydroxide, ammonium carbonate, or ammonia gas to raise the pH of said slurry to at least 6.0, washing the thus neutralized hydrous oxide to remove the ammonium sulphate formed until the sulphur content, calculated as % S falls within the range of from 0.03% to 0.3% on a dry titanium dioxide weight basis, drying said washed hydrous oxide at 250°C—700°C until soft aggregates of crystals of titanium dioxide having an average individual particle size which falls within the range of from 100 to 500 Å are formed, and grinding said aggregates to a fine powder.

It is desirable to define what is meant by "photoreactivity". A photoreactive material is one which will react in a light sensitive system

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and in particular a copy paper system to form an image when exposed to ultraviolet illumination.

5 The titanium dioxide products obtained were tested for photoreactivity by the mandelic acid test as follows:

10 g of the titanium dioxide are mixed with a sufficient amount of aqueous 0.5 M mandelic acid solution to form a soft paste. The paste 10 is placed upon a microscope slide glass plate (5 in. x 5 in. x 1mm), covered with a thick glass plate (5 in. x 5 in. double strength window glass), and pressed to distribute the paste over an area about 3 inches in diameter; 15 microscope slides (1 in. x 3 in. x 1 mm) are used between the plates as spacers. The edges of the plates are bound together with 1 inch tape to prevent evaporation. The initial reflectance of the paste through the microscope slide glass plate is measured by means 20 of a Colormaster Differential Colorimeter with the green filter. The plates are placed on a rotating turntable, microscope slide glass plate side up, underneath three sunlamps (275 watts) 25 arranged in an equilateral triangle 13 inches from centre to centre approximately 13 inches above the turntable. Before each run the ultraviolet intensity from the lamp is measured and weak lamps are replaced. Reflectance 30 measurements are made at suitable intervals and the change in percent reflectance with time is determined. This figure is a measure of the photoreactivity of the titanium composition. A change in reflectance of at least 5 units 35 in 10 minutes is required as the minimum acceptable for commercial applications.

40 The preparation of the hydrous titanium dioxide in the first step of the present invention may be carried out by any of the well-known hydrolysis methods described in the prior art. In such processes a titanium sulphate-ferrous sulphate solution is formed by digesting a titaniferous iron ore in concentrated sulphuric acid to form a so-called "digestion cake" 45 which is dissolved in water or dilute acid. Such a solution, after clarifying and concentrating, is then subjected to hydrolysis by diluting and boiling to precipitate the titanium values. The hydrous titanium oxide formed is then filtered, bleached and washed to remove the ferrous sulphate and other colouring impurities. Such a hydrous titanium oxide even after thorough washing contains from 5% to 15% H<sub>2</sub>SO<sub>4</sub>, combined or adsorbed in the composition.

55 In order to prepare the product of the present invention it is necessary to reduce the amount of H<sub>2</sub>SO<sub>4</sub> present in the hydrous oxide. Ammonia gas, ammonium hydroxide or ammonium carbonate is then added to an 60 aqueous slurry of the hydrous titanium oxide to form ammonium sulphate which can be readily removed by washing. The amount of ammonium compound added is the amount necessary to raise the pH of the hydrous titanium oxide slurry to at least 6.0. Raising

the pH to above 8.0 does not further improve the product but merely adds to the cost of the process.

70 After adding the appropriate amount of ammonium compound, the hydrous titanium oxide is then de-liquored and washed until the percentage of sulphate in the dried product is 0.03% to 0.3%, calculated as S on a dried titanium dioxide weight basis.

75 After washing, the neutralized hydrous oxide is then dried at a temperature from 250°C to 700°C until the average particle size of the titanium dioxide crystals formed falls within the range of from 100 to 500 angstroms. The dried product is then ground to break up 80 the soft aggregates which form during the drying step.

85 The ground product was then analysed to determine the various characteristics.

90 The average particle size was determined by X-ray diffraction analysis, using the "line broadening" technique. This is a well known X-ray diffraction technique for measuring size of particles having poorly defined crystal structure, and is based upon a volume measurement, rather than number or weight.

95 The moisture content of the product was determined by heating 1 gram sample of the product at 750°C. for 1 hour and determining the loss in weight.

#### EXAMPLE 1.

100 A hydrous titanium oxide was prepared by adding a titanium sulphate-ferrous sulphate solution to hot water and boiling the mixture. The titanium sulphate solution used had the following analysis:

TiO <sub>2</sub>	250 g.p.l.
H <sub>2</sub> SO <sub>4</sub>	500 g.p.l.
FeSO <sub>4</sub>	169 g.p.l.
H <sub>2</sub> SO <sub>4</sub> /TiO <sub>2</sub>	2.0
Spec. Gravity	1.675 at 60°C.

105 3000 ml. of this titanium sulphate solution heated to 96°C. were added to 750 ml. water heated to 96°C. within a period of 16 minutes. The entire mixture was then heated to boiling, and boiled for 3 hours to complete the hydrolysis. 790 ml. of hot water were added to the mixture to cut the concentration to 165 g.p.l. TiO<sub>2</sub>.

110 115 The resulting hydrous titanium oxide was filtered, washed free of soluble iron salts, bleached with 10% H<sub>2</sub>SO<sub>4</sub> and 0.1% aluminum metal for 1 hour at 80°C. at 20% solids, then filtered and washed with water until iron-free. The washed filter cake contained 10% H<sub>2</sub>SO<sub>4</sub>, calculated on a TiO<sub>2</sub> basis. 2143 grams of the filter cake containing 35% solids were admixed with 1607 ml. water to form from a slurry containing 20% solids. 120 with agitation 159 grams of ammonium hydroxide diluted with 178 ml. water were added to the hydrous oxide slurry at 60°C. to raise the pH of the slurry to 7.1.

5	The neutralised solids were filtered and the solids were washed with 15 litres water and then dried at a temperature of 350°C. for 1½ hours as a consequence of which the moisture content of the material was reduced to 6.2%. The dried material was then steam milled.	30
10	The dried and milled titanium dioxide had the following properties:	35
	H <sub>2</sub> O 6.2%	
	S 0.11%	
	Average Particle Size 177 Å	
	Surface Area >200 m <sup>2</sup> /g	
	Reflectance Loss in 2 min. 26	
	Reflectance Loss in 10 min. 38	
15	The operational details and results obtained are also recorded in the following table. This photoreactive titanium dioxide was used in aqueous copy paper system and an excellent image was obtained.	40
20	EXAMPLE 2.	45
25	In this run the procedure of Example 1 was repeated except that the pH of the slurry was raised to 6.3. The operational details and the results obtained are recorded in the following table along with those of Example 1. This product also produced an excellent image in a copy paper system.	50
	EXAMPLES 3—4.	55
	These runs were carried out as controls using the procedure of Example 1 except that the amount of ammonium hydroxide used was less than that required to raise the pH of the slurry to 6.0. In Example 3 the pH was raised only to 5.5 while in Example 4 none of the H <sub>2</sub> SO <sub>4</sub> was neutralised. The results are recorded in the table. These titanium dioxide products contained excessive amounts of sulphur and water. The pH was also too low on both products. When used in copy paper, the images were of poor quality.	
	EXAMPLES 5—10	
	In these runs the procedure of Example 1 was repeated except that the neutralized hydrous titanium oxide were dried at various temperatures, i.e. from 280°C. to 650°C. All of these products were useful in preparing images. The operational details and results obtained are recorded in the table.	
	EXAMPLES 11—12	
	In these runs the procedure of Example 1 was used except that ammonia gas and ammonium carbonate were used in place of ammonium hydroxide. In both of these examples the products obtained were substantially identical to product obtained in Example 1.	

TABLE

Example No.	1	2	3	4
pH of Neutralised Slurry	7.1	6.3	5.5	2.3
Drying Temp. °C.	350	350	350	350
Drying Time, hrs.	1.5	1.5	1.5	1.5
% S	0.11	0.29	0.92	1.8
% Moisture	6.2	6.8	12.4	17.6
Surface Area m <sup>2</sup> /g	>200	>175	>175	>175
Ave. Part. Size, Å	177	163	114	84
Loss in Reflectance in 2 min.	26	22	(poor quality print)	(poor quality print)
Loss in Reflectance in 10 min.	38	44		

TABLE (Cont.)

Example No.	5	6	7	8
pH of Neutralised Slurry	7.1	7.1	7.1	7.1
Drying Temp. °C.	280	320	380	450
Drying Time, hrs.	1.5	1.5	1.5	1.5
% S	0.11	0.13	0.13	0.12
% Moisture	9.0	6.8	5.7	4.7
Surface Area m <sup>2</sup> /g.	>175	>175	>175	>150
Ave. Part. Size, Å	137	149	195	233
Loss in Reflectance in 2 min.	20	16	15	—
Loss in Reflectance in 10 min.	39	34	37	37

Example No.	9	10
pH of Neutralised Slurry	7.1	7.1
Drying Temp. °C.	550	650
Drying Time, hrs.	1.5	1.5
% S	0.11	0.11
% Moisture	4.1	3.1
Surface Area m <sup>2</sup> /g.	115	83
Ave. Part. Size, Å	245	357
Loss in Reflectance in 2 min.	8	13
Loss in Reflectance in 10 min.	32	36

## WHAT WE CLAIM IS:—

1. Photoreactive titanium dioxide having the crystal structure of anatase comprising finely divided particles having an average individual particle size from 100 to 500 angstroms; a sulphur content calculated as percent S which falls within the range of from 0.03% to 0.3% on a dry titanium dioxide weight basis; a surface area from 60 to 250 square meters per gram; a moisture content from 2% to 10% and a photoreactivity, measured by the mandelic acid test hereinbefore described, as a change in reflectance, of at least 5 units in 2 minutes when exposed to ultraviolet radiation.

2. Method for preparing a photoreactive titanium dioxide which comprises: hydrolyzing a titanium sulphate-iron sulphate solution to form hydrous titanium oxide, filtering

bleaching and washing said hydrous oxide to remove the soluble iron salts therefrom, said bleached hydrous oxide being substantially iron-free but containing from 5% to 15% H<sub>2</sub>SO<sub>4</sub> associated with said hydrous oxide, forming an aqueous slurry of said bleached hydrous oxide, treating said slurry with a sufficient amount of ammonium hydroxide, ammonium carbonate or ammonia gas to raise the pH of said slurry to at least 6.0, washing said neutralized hydrous oxide to remove the ammonium sulphate formed until the sulphur content calculated as % S falls within the range of from 0.03% to 0.3% on a dry titanium dioxide weight basis, drying said washed hydrous titanium oxide at 250°C—700°C until soft aggregates of crystals of titanium dioxide having an average individual particle size which falls within the range of from 100

to 500 angstroms are formed, and grinding said aggregates to a fine powder.

3. A process for the production of photo-reactive titanium dioxide substantially as 5 herein described in any one of Examples 1, 2 and 5 to 10.

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